

Korea Polymer Journal

Volume 8, Number 2 April 30, 2000

© Copyright 2000 by The Polymer Society of Korea

Solvent Effects on the Structure of Resorcinol Formaldehyde Resin

Sung-Seen Choi

Kumho Research and Development Center, 555 Sochon-dong, Kwangsan-gu, Kwangju 506-040, Korea

Received December 9, 1999

Abstract : Stabilities and structures of resorcinol formaldehyde resins (RF resins) and their dependence on solvent were studied by molecular mechanics and molecular dynamics. Dimers to decamers of the RF resins in the conditions of dielectric constant = 1.00, 21.01, 36.64, and 80.10 were calculated. The average distance between oxygen atoms in 1-hydroxyl groups of adjacent resorcinols of the resins became longer with increased dielectric constant of the environment. The number of intramolecular hydrogen bonds of the resins decreased by increasing the dielectric constant of the environment. The RF resin structure on the surface of fabric or steel cord was explained based on the present calculation.

Introduction

Phenolic resins produced by the reaction of phenols and aldehydes are interesting materials because of their high thermal stability, excellent resistance to combustion, high dimensional stability, good mechanical properties, and high chemical stability.¹⁻⁹ Casiraghi and coworkers⁸ synthesized all-ortho phenol acetaldehyde novolak resins with uniform constituents *via* bromomagnesium ion mediated reaction. Phenolic resins are widely used depending on their types as bonding agents,¹⁰ tackifiers,^{9,11} vulcanizing agents,¹² photoresists,¹³ and

so forth.

Resorcinol formaldehyde resin (RF resin) is synthesized by polycondensation of resorcinol with formaldehyde.^{14,15} The RF resin is used as a bonding agent in adhesion between rubber and fabric/steel cord. Resorcinol formaldehyde latex (RFL) adhesive systems are used to bond synthetic fibers to rubber compounds. The adhesive was applied primarily to rayon fibers and later extended to nylon and glass fibers. The RFL treated fibers are used to reinforce rubber products such as tires, conveyor belts, hoses, and V-belts.

Conformation of a molecule depends on the environmental condition such as dielectric constant.¹⁶ Rio and coworkers¹⁶ studied variation of

*e-mail : sschoi@swan.kumho.co.kr

structure of ozonolysis reaction intermediate depending on the environment which is established with different dielectric constants. In the present work, the solvent effect on energetical stability and structure of the resorcinol formaldehyde resin was studied by molecular mechanics and molecular dynamics. The various solvent environments were established by using different dielectric constants. Figure 1 gives general formula of the resorcinol formaldehyde novolak resin.

Modeling and Calculation

The initial structures of input molecules were generated by the *Insight II* package of MSI. 2-Methylresorcinol was used as a repeat unit. The input molecules were constructed by linking the repeat unit (2, 6-polycondensation) with head-to-tail orientation. General formula of the resorcinol formaldehyde resin is shown in Figure 1. The $n = 1, 2, 3, \dots$ indicates dimer, trimer, tetramer, ..., respectively. Dimers to decamers of the RF resin were calculated. Calculations were carried out by molecular mechanics and dynamics with CFF91 force field.¹⁷ The CFF91 force field employs a quadratic polynomial for bond stretching and angle bending, and a three-term Fourier expansion for torsions. The out-of-plane coordinate is defined according to Wilson *et al.*¹⁸ All the cross terms up to the third order that have been found to be important are also included. Coulombic interaction between atomic charges and van der Waals interactions using the inverse 9th-power term for the repulsive part rather than the more typical 12th-power term are employed. Potential cutoff distance of 10.0 Å was employed. In order to investigate the influence of solvent on energetical stability and structure of the RF resin, various dielectric con-

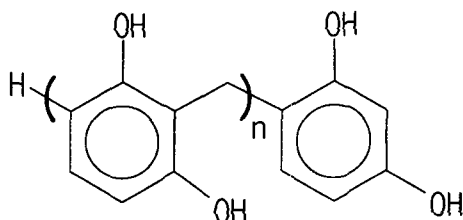


Figure 1. General formula of resorcinol formaldehyde resin.

stants (ϵ) of 1.00 (vacuum), 21.01 (acetone), 36.64 (aceto-nitrile), and 80.10 (water) were used. The energy-minimized structures of the RF resins were obtained by conformational search. The conformational search was done by the annealing technique consisting of 200 ps molecular dynamics at 900K and 200 samples obtained each 1000 fs (1 ps) for further minimization. Of the 200 conformers, the conformer with the lowest energy was determined as the energy-minimized structure.

Results and Discussion

The energy-minimized structures of the RF resins obtained from the conformational search were shown in Figures 2-5. Figures 2, 3, 4, and 5 give the skeletal structures of pentamers of the RF resin obtained under the condition of dielectric constants $\epsilon = 1.00, 21.01, 36.64,$ and $80.10,$ respectively. The molecular structures were displayed with only oxygen and carbon atoms, where solid and open circles denote oxygen and carbon atoms, respectively. The RF resins, irrespective of dielectric constants, have common structural characteristics of intramolecular hydrogen bond between the hydroxyl groups. Of the intramolecular hydrogen bonds, the major ones are the hydrogen bond between 1-hydroxyl groups of the

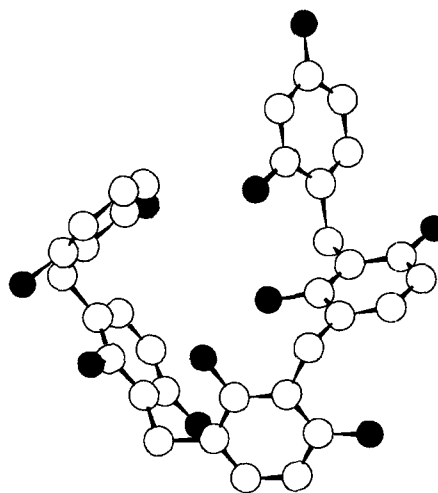


Figure 2. Skeletal structure of the energy-minimized resorcinol formaldehyde resin pentamer obtained from calculation in $\epsilon = 1.00$. Solid and open circles indicate oxygen and carbon atoms, respectively.

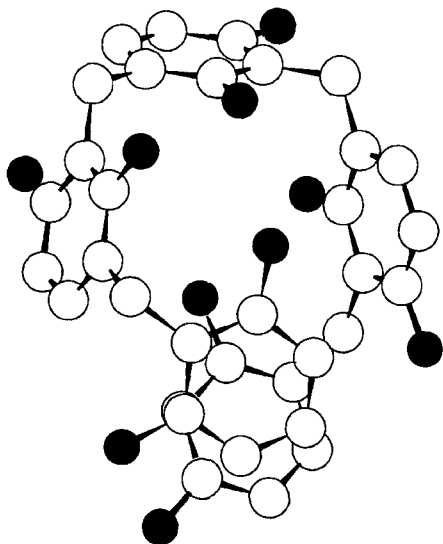


Figure 3. Skeletal structure of the energy-minimized resorcinol formaldehyde resin pentamer obtained from calculation in $\epsilon = 21.01$. Solid and open circles indicate oxygen and carbon atoms, respectively.

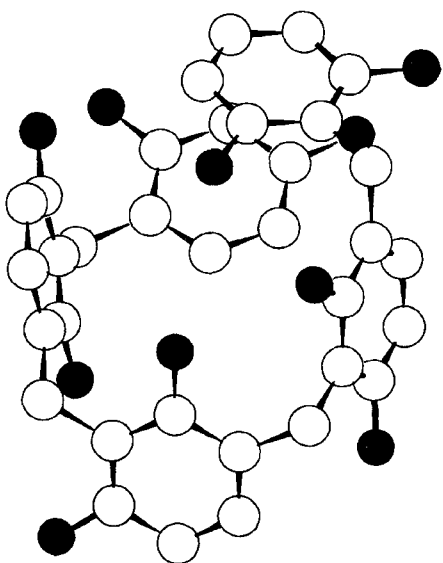


Figure 4. Skeletal structure of the energy-minimized resorcinol formaldehyde resin pentamer obtained from calculation in $\epsilon = 36.64$. Solid and open circles indicate oxygen and carbon atoms, respectively.

adjacent resorcinols. The intramolecular hydrogen bond of phenolic formaldehyde resin was studied by several groups.^{6,13} Paulus and Böhmer⁶ studied the crystal structures of *p*-alkylphenol

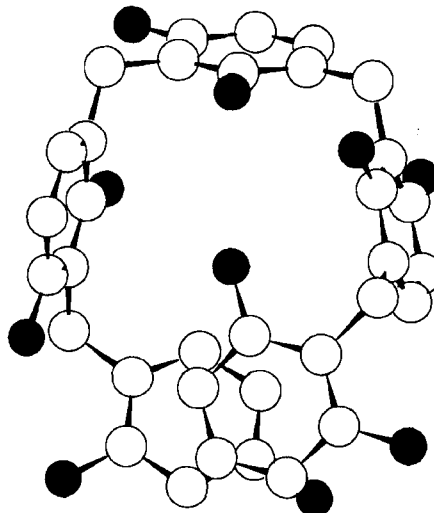


Figure 5. Skeletal structure of the energy-minimized resorcinol formaldehyde resin pentamer obtained from calculation in $\epsilon = 80.10$. Solid and open circles indicate oxygen and carbon atoms, respectively.

formaldehyde resin tetramer with hydrogen, methyl, and *t*-butyl as the *p*-substituent by single crystal X-ray analysis and found the existence of the intramolecular hydrogen bond between hydroxyl groups of the adjacent phenolic units. Templeton and coworkers¹³ studied the intramolecular hydrogen bonded phenol formaldehyde resin dimer-tetramer by molecular mechanics energy minimization techniques, which was consistent with X-ray crystallography data.

In order to investigate the structural difference of the resins depending on the dielectric constant, the distance between the oxygen atoms of 1-hydroxyl groups of adjacent resorcinols, r_{oo} , were measured from the energy-minimized structures of the resins. Table I gives the r_{oo} of dimer to decamer of the energy-minimized RF resins. The average r_{oo} from dimer to decamer of the resins in the condition of $\epsilon = 1.00$ is shorter than those in the other dielectric constants by about 0.14–0.65. The average r_{oo} of the resins increases by increasing the dielectric constant except the resins in $\epsilon = 21.01$. The average r_{oo} of the resins are 3.33, 3.98, 3.47, and 3.86 for $\epsilon = 1.00$, 21.01, 36.64, and 80.10, respectively.

The number of intramolecular hydrogen bonds is one of principal factors to characterize the

Table I. Distance between Oxygen Atoms of the 1-Hydroxyl Groups of Adjacent Resorcinols in the Energy-minimized Resorcinol Formaldehyde Resins in Å

Size of Molecule	$\epsilon = 1.00$	$\epsilon = 21.01$	$\epsilon = 36.64$	$\epsilon = 80.10$
Dimer	3.08	3.27	3.25	3.23
Trimer	3.04 - 3.10	3.15 - 4.62	3.16 - 4.55	3.19 - 4.16
Tetramer	2.96 - 2.90 - 2.88	3.30 - 3.22 - 4.16	3.43 - 4.45 - 4.77	3.44 - 4.49 - 4.77
Pentamer	2.92 - 2.96 - 3.05 - 2.97	3.12 - 3.03 - 4.41 - 3.25	3.20 - 3.01 - 4.45 - 5.82	3.27 - 3.02 - 4.42 - 5.87
Hexamer	2.82 - 2.86 - 2.93 - 4.42 - 3.09	3.26 - 3.95 - 4.82 - 3.03 - 5.64	3.02 - 5.65 - 4.55 - 3.19 - 4.32	3.11 - 4.99 - 4.24 - 5.72 - 3.29
Heptamer	3.17 - 3.29 - 2.98 - 2.94 - 4.45 - 3.17	3.01 - 3.01 - 4.94 - 3.95 - 3.28 - 3.71	2.96 - 2.84 - 3.79 - 3.04 - 3.09 - 5.41	3.06 - 3.13 - 3.51 - 3.07 - 3.76 - 5.56
Octamer	2.99 - 2.88 - 4.65 - 3.71 - 3.05 - 5.05 - 3.25	3.16 - 3.00 - 3.04 - 4.70 - 5.38 - 5.72 - 5.74	3.12 - 3.23 - 3.66 - 2.96 - 3.07 - 2.99 - 4.75	2.98 - 3.03 - 3.14 - 3.65 - 3.24 - 3.26 - 3.24
Nonamer	2.98 - 2.88 - 4.21 - 3.50 - 3.03 - 3.00 - 2.88 - 5.74	2.98 - 5.77 - 4.09 - 3.99 - 3.71 - 4.93 - 3.26 - 4.49	3.07 - 2.91 - 3.09 - 2.92 - 5.73 - 3.26 - 4.59 - 3.34	3.00 - 5.17 - 3.57 - 5.78 - 4.84 - 4.17 - 3.86 - 5.04
Decamer	3.04 - 3.15 - 2.92 - 3.00 - 5.77 - 3.61 - 2.93 - 2.78 - 3.02	3.75 - 4.29 - 5.50 - 4.69 - 3.17 - 3.29 - 5.64 - 3.85 - 3.06	3.18 - 4.48 - 3.36 - 3.36 - 4.25 - 2.96 - 3.44 - 3.11 - 2.95	3.27 - 2.94 - 3.03 - 2.87 - 5.38 - 4.04 - 4.58 - 3.16 - 3.17

chemical structure of the resin. Thus, the number of intramolecular hydrogen bonds of the energy-minimized RF resins was counted. Table II gives the number of intramolecular hydrogen bonds of the resins from dimers to decamers. The number of intramolecular hydrogen bonds of the resin in $\epsilon = 1.00$ increase from 1 to 9 by increasing the molecular size from dimer to decamer. The maximum numbers of the intramolecular hydrogen bonds of the resins for the case of $\epsilon = 21.01$, 36.64, and 80.10 do not exceed 4, 6, and 4, respectively. The total number of the intramolecular hydrogen bonds in the resins from dimer to decamer decreases by increasing the dielectric constant. The total numbers of the the intramolecular hydrogen bonds of the resins are 46, 25, 24, and 19 for $\epsilon = 1.00$, 21.01, 36.64, and 80.10, respectively. The number of intramolecular hydrogen bond of the resins in $\epsilon = 1.00$ is about twice larger than those of the resins in $\epsilon = 21.01$, 36.64, and 80.10. This implies that the polar environment prevent the RF resins from hydrogen-bonding. The polar solvent can build intermolecular hydrogen bond with the RF resin so that the intramolecular hydrogen bond of the resins is inhibited by the solvation of hydroxyl groups of the resorcinol of the resins with polar

Table II. Number of Hydrogen Bonds between Hydroxyl Groups of the Resorcinols in the Energy-minimized Resorcinol Formaldehyde Resins

Size of Molecule	$\epsilon = 1.00$	$\epsilon = 21.01$	$\epsilon = 36.64$	$\epsilon = 80.10$
Dimer	1	1	1	1
Trimer	2	1	1	1
Tetramer	4	1	2	3
Pentamer	5	3	2	1
Hexamer	5	4	2	2
Heptamer	6	4	3	3
Octamer	6	4	3	4
Nonamer	8	4	6	2
Decamer	9	3	4	2

solvent.

Total energies of the energy-minimized resins were calculated to investigate the relative stability of the resins depending on the dielectric constant of the environment. Figure 6 shows the variation of the total energy of the energy-minimized resin structure with the number of the repeat unit. The total energies of the resins in $\epsilon = 1.00$ are much lower than those of the resins in $\epsilon = 21.01$, 36.64, and 80.10. This implies that the RF resins have a more stable structure in vacuum than in polar solvents. This may be due to the number of the intramolecular hydrogen bonds of the resins and

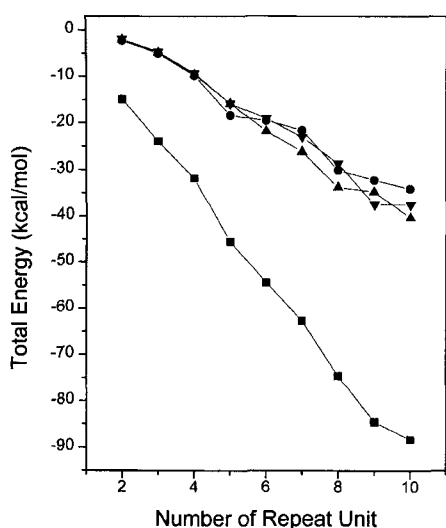


Figure 6. Variation of total energy of the energy-minimized structure of resorcinol formaldehyde resins as a function of the repeat unit in different dielectric environment. Rectangles, circles, up-triangles, and down-triangles indicate $\epsilon = 1.00, 21.01, 36.64,$ and $80.10,$ respectively.

the distances between oxygen atoms of 1-hydroxyl groups of the adjacent resorcinols. The number of the intramolecular hydrogen bond of the resins in vacuum ($\epsilon = 1.00$) is much larger than those of the resins in polar solvents and the distances between oxygen atoms of 1-hydroxyl groups of the adjacent resorcinols in vacuum are shorter than those in the solvents as discussed previously. The variation of the total energy of the resin with the type of solvent can be explained by the distances between oxygen atoms of 1-hydroxyl groups of the adjacent resorcinols rather than by the number of the intramolecular hydrogen bonds of the resins. The RF resins in $\epsilon = 36.64$ and 80.10 are, on the whole, energetically more stable than those in $\epsilon = 21.01$ although the numbers of intramolecular hydrogen bonds of the resins in $\epsilon = 36.64$ and 80.10 are smaller than that in $\epsilon = 21.01$. The r_{oo} values of the resins in $\epsilon = 36.64$ and 80.10 are shorter than those in the $\epsilon = 21.01$. This is consistent with the total energy.

Many rubbery products contain textile reinforcements for high strength and dimensional stability. These composites can perform optimally if the adhesion between reinforcement and rubber is strong. The classical way to obtain good adhe-

sion between rayon (cellulose) or nylon fiber to rubber is to dip the cords in resorcinol formaldehyde latex (RFL) suspension.¹⁹ Adhesion between fabric cord and rubber is accomplished by formation of chemical bond between them by the RF resin. Since rayon and nylon fibers have many polar groups such as CO-, -NH-, and -OH, surface of the fabric cords is polar so hydrogen bond between the surface and polar chemicals can be formed with ease. Thus, the RF resin can be formed hydrogen bond with the fabric cords with ease because of many hydroxyl groups in the RF resin. Because of the high surface polarities of rayon and nylon, it can be considered that the RF resin structure on the fabric cord surface is similar to the structure in the environment of a high dielectric constant. Adhesion of vulcanized rubber to brass-coated steel cords is of vital importance to the long-term durability of steel-belted radial tires. The two most widely used adhesion promoters used in industry are based on the condensation chemistry of RF resin, a methylene acceptor, with active methylene donors such as hexamethoxymethylmelamine (HMMM).²⁰ Cured resins enhance reinforcement and improve the interfacial adhesion. The RF resin structure obtained from the current calculations can explain the reaction between the RF resin and HMMM. Since the steel cord has a high polar surface, the resin structure on the steel cord surface will be also less packed as similar to the structure in the environment of a high dielectric constant. If the resin has the loose structure, the active site to react with HMMM will be exposed to some extent. Thus, the exposed active site can react easily with HMMM.

References

- (1) A. Knop and L. A. Pilato, in *Phenolic Resins*, Springer-verlag, Berlin, 1985.
- (2) M. F. Grenier-Loustalot, S. Larroque, D. Grande, P. Grenier, and B. Didier, *Polymer*, **37**, 1363 (1996).
- (3) M. F. Grenier-Loustalot, S. Larroque, P. Grenier, and B. Didier, *Polymer*, **37**, 639 (1996).
- (4) C. D. Gutsche, B. Dhawan, K. H. No, and R. Muthukrishnan, *J. Am. Chem. Soc.*, **103**, 3782 (1981).
- (5) R. Lamartine, *Plast. Rubber Proc. Appl.*, **6**, 313 (1986).
- (6) E. Paulus and V. Böhmer, *Makromol. Chem.*, **185**,

- 1921 (1984).
- (7) G. Casiraghi, M. Cornia, G. Sartori, G. Casnati, V. Bocchi, and G. D. Andreetti, *Makromol. Chem.*, **183**, 2611 (1982).
- (8) G. Casiraghi, M. Cornia, G. Ricci, G. Casnati, G. D. Andreetti, and L. Zetta, *Macromolecules*, **17**, 19 (1984).
- (9) L. E. Gwin and E. J. Weaver, *J. Elast. Plast.*, **9**, 289 (1977).
- (10) G. R. Hamed and J. Huang, *Rubber Chem. Technol.*, **64**, 285 (1991).
- (11) F. L. Magnus and G. R. Hamed, *Rubber Chem. Technol.*, **64**, 65 (1991).
- (12) M. Duin and A. Souphanthong, *Rubber Chem. Technol.*, **68**, 717 (1995).
- (13) M. K. Templeton, C. R. Szmanda, and A. Zampini, *Proc. SPIE*, **771**, 136 (1987).
- (14) R. W. Pekala, *J. Mat. Sci.*, **24**, 3221 (1989). S. A. Letts, S. R. Buckley, F. M. Kong, E. F. Lindsay, and M. L. Sattler, *Mat. Res. Soc. Symp. Proc.*, **177**, 275 (1990).
- (16) E. Rio, P. Aplincourt, M. F. Ruiz-Lopez, *Chem. Phys. Lett.*, **280**, 444 (1997).
- (17) J. R. Maple, U. Dinur, and A. T. Hagler, *Proc. Nat. Acad. Sci. USA*, **85**, 5350 (1988). E. B. Wilson, J. C. Decius, and P. C. Cross, in *Molecular Vibrations*; Dover, New York, 1980.
- (19) B. Rijpkema, and W. E. Weening, *Rubber World*, **210(6)**, 26 (1994).
- (20) B. Singh, and J. E. Sedlak, *Rubber World*, **210(6)**, 32 (1994).